

PB86-145620

Control of Cadmium Carbonate
Precipitation Interferences during the
Dialysis of Cadmium in High Bicarbonate
Alkalinity Aquatic-Life Bioassay Waters

(U.S.) Environmental Research Lab.-Duluth, MN

Dec 85



U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-145620

EPA/600/3-86/001
December 1985

Control of Cadmium Carbonate Precipitation Interferences During the Dialysis
of Cadmium in High Bicarbonate Alkalinity Aquatic-Life Bioassay Waters

by

John E. Poldoski

U.S. Environmental Protection Agency
Environmental Research Laboratory-Duluth
6201 Congdon Boulevard
Duluth, Minnesota 55804

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/3-86/001		2.		3. RECIPIENT'S ACCESSION NO. 886 T4562075	
4. TITLE AND SUBTITLE Control of Cadmium Carbonate Precipitation Interferences During the Dialysis of Cadmium in High Bicarbonate Alkalinity Aquatic-Life Bioassay Waters				5. REPORT DATE December 1985	
7. AUTHOR(S) J. E. Poldoski				6. PERFORMING ORGANIZATION CODE	
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Environmental Research Laboratory-Duluth 6201 Congdon Boulevard Duluth, MN 55804				8. PERFORMING ORGANIZATION REPORT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Duluth, MN 55804				10. PROGRAM ELEMENT NO.	
15. SUPPLEMENTARY NOTES				11. CONTRACT/GRANT NO.	
				13. TYPE OF REPORT AND PERIOD COVERED	
16. ABSTRACT The precipitation of cadmium carbonate during the dialysis of cadmium in a high bicarbonate alkalinity natural water, was linked to a significant source of error when determining dialyzate cadmium concentrations. The relative standard deviation was reduced by approximately four-fold when this precipitation was controlled by adding a particular preparation of humic acid to the dialysis bag filling solution. Linear regression correlation coefficients for sample-by-sample comparisons between resultant dialysis values and corresponding free cadmium values, obtained by cadmium ion selective electrode, were 0.90 or greater for concentrations in the range of 2 ug/L to 132 ug/L Cd ²⁺ .				14. SPONSORING AGENCY CODE EPA-600/03	
				17. KEY WORDS AND DOCUMENT ANALYSIS	
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group	
18. DISTRIBUTION STATEMENT Release to public		19. SECURITY CLASS (This Report) Unclassified		21. NO. OF PAGES 32	
		20. SECURITY CLASS (This page) Unclassified		22. PRICE	

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

The precipitation of cadmium carbonate during the dialysis of cadmium in a high bicarbonate alkalinity natural water, was linked to a significant source of error when determining dialyzate cadmium concentrations. The relative standard deviation was reduced by approximately four-fold when this precipitation was controlled by adding a particular preparation of humic acid to the dialysis bag filling solution. Linear regression correlation coefficients for sample-by-sample comparisons between resultant dialysis values and corresponding free cadmium values, obtained by cadmium ion selective electrode, were 0.90 or greater for concentrations in the range of 2 $\mu\text{g/L}$ to 132 $\mu\text{g/L}$ Cd^{2+} .

CONTENTS

	<u>Page</u>
Disclaimer	ii
Abstract	iii
Conclusions	v
Recommendations	vi
Figures	vii
Tables	viii
Acknowledgment	ix
Introduction	1
Experimental Section	2
Apparatus	2
Chemicals and Reagents	2
Quenching Reagent Preparation	3
Procedure	3
Results and Discussion	5
Reproducibility at High and Low Alkalinity	8
Quenching Effect of Humic Acid	10
Effect of Variables on the Conditional Concentration Factor (F)	10
Comparison to Measurements via Cadmium ISE	16
Literature Cited	20

CONCLUSIONS

1. Precipitation of CdCO_3 in the high bicarbonate alkalinity bioassay water was a cause of variability in the dialysis of cadmium.
2. Aldrich humic acid markedly quenched the rate of cadmium carbonate precipitation.
3. The presence of the quenching reagent in the dialyzate markedly improved precision when compared to experiments without its presence.
4. A highly significant correlation of Cd^{2+} concentration in bioassay waters ($R = 0.9$) was obtained between dialysis and ion selective electrode potentiometry.
5. Alteration of equilibria in the dialyzate by the presence of the quenching reagent can be corrected by performing the appropriate preliminary measurements.

RECOMMENDATIONS

1. Additional research should be undertaken to identify alternative quenching reagents which would not significantly alter the equilibria of the dialyzate and still prevent CdCO_3 precipitation.
2. Environmental situations should be investigated where application of quenching reagents may be of benefit.
3. Studies on the prevention of precipitation in dialyzates should be extended to other metals.
4. The use of quenching reagents to aid in metal-complexometric titrations of natural waters should be investigated.

FIGURES

	<u>Page</u>
Figure 1. Water quality variables affecting the pseudo first-order rate constant (arbitrary units) for loss of free cadmium from solution.	6
Figure 2. Change in mean 5 h normalized conditional concentration factor as a function of dialysis time for retentate solutions A and B.	7
Figure 3. Change in mean 4 h normalized conditional concentration factor as a function of dialysis time for high bicarbonate alkalinity flow-through bioassay waters.	13
Figure 4. Calculated and mean experimental values of F for retentate solution B and the 1,000 MWCO membrane.	15
Figure 5. Correlation of values obtained by dialysis and ISE.	17

TABLES

	<u>Page</u>
Table I. Reproducibility of 5 h dialyses in various carbonate alkalinity waters using deionized distilled water as the dialysis bag filling solution.	9

ACKNOWLEDGMENT

The author thanks D. Benoit, V. Mattson and S. Heinritz for maintaining the mini-diluter system.

INTRODUCTION

Research papers (1-4) have appeared recently concerning the use of dialysis for investigating the metal ion binding properties of natural waters and the dissolved state of metal ions. In particular, Truitt and Weber (4) have reported using equilibrium dialysis for studying binding from macromolecular natural organics found in several bodies of water of the northeastern U.S., but they noted some interferences, presumably associated with metal carbonate precipitation within the dialysis bag. In the work presented here, some similar problems in the dialysis of cadmium occurred which were linked to cadmium carbonate precipitation in a high bicarbonate alkalinity water that was used for conducting aquatic-life bioassays in this laboratory. In other related chemical kinetics studies of cadmium precipitation in this water, it was discovered that the presence of Aldrich humic acid (HA) drastically reduced this rate of precipitation. Thus, it followed that this observation could be put to constructive use. If an appropriate preparation of humic acid (quenching reagent) was incorporated as part of the filling solution for the dialysis bag, it should be largely incapable of permeating the membrane and into the retentate solution. Therefore, it would be available within the dialysis bag to control cadmium carbonate precipitation. The purpose of this paper is to report on this novel approach to dialysis in natural waters and illustrate some of its characteristics.

EXPERIMENTAL SECTION

Apparatus. Experiments were conducted using two different molecular weight cut-off (MWCO) dialysis bags (Spectrum Medical Industries, SMI), specifically the 1,000 MWCO (#132634) and 12,000-14,000 MWCO (#132700) sizes clamped with SMI closures.

The flow-through mini-diluters were operated as part of an aquatic-life related study in this laboratory and details of this work, including functioning of the mini-diluters are described elsewhere (5,6).

Atomic absorption spectrometric (AAS) measurements of total cadmium and other elements were made with a Perkin Elmer model 5000 atomic absorption spectrophotometer equipped with deuterium arc background correction, a model HGA-500 graphite furnace, a model AS-40 autosampler, a model AS-50 auto-sampler, and a model 56 strip chart recorder.

Free cadmium ion and pH measurements were made with an Orion model 801 pH meter equipped with a 500 mL FEP teflon cell, an Orion model 9448A cadmium ion selective electrode (ISE), an Orion double junction reference electrode (#900200), an Orion model 605 electrode switch, and a Perkin Elmer model 165 strip chart recorder.

Calculations were performed with a Texas Instruments model TI59 programmable calculator equipped with the statistics solid-state software module.

Chemicals and Reagents. Unless indicated otherwise, all chemicals were of reagent grade quality or better and deionized distilled water (Millipore Super Q) was used for preparing solutions. The high calcium hardness-high bicarbonate alkalinity natural water (hardwater), used as the dilutant water for aquatic-life bioassays, was prepared by dissolving CaCO_3 from limestone (5,7) in Lake Superior water (softwater) followed by filtration. It was subsequently aerated with 0.45 μ filtered air until a constant pH of

approximately 8.2 was maintained. Typical total concentrations for cations and anions were very similar to that reported elsewhere for Lake Superior (8-10), with the exception of trace element concentrations listed in reference 10. Hardwater represented a four to five-fold increase in total CaCO_3 hardness and alkalinity over the values for softwater, specifically: 48 mg/L versus 205 mg/L for total hardness and 48 mg/L versus 212 mg/L for total alkalinity.

AAS and ISE standards were prepared from high purity chemicals and their nominal values agreed to within 2% or better with U.S. Environmental Protection Agency trace metal reference samples.

Quenching Reagent Preparation. The quenching reagent was prepared by adding 1,000 mg of humic acid (Aldrich, H1675-2) to one liter of hardwater and shaking the mixture for 1 h. Portions of this solution were then pressure-filtered at 3 atm through a precleaned Millipore 0.45 μ , 47 mm diameter membrane filter. The 0-10 mL fraction was discarded and the 10-50 mL fraction was collected and saved. This filtration process was repeated with a new filter until the entire 1 L volume was processed. The collected filtrate was diluted ten-fold with deionized distilled water and stored in the absence of light at 4°C until use.

Procedure. Dialysis bags were cleaned according to a procedure given by Truitt and Weber (3) and they were stored refrigerated in 0.5% v/v HNO_3 . Before use, they were thoroughly soaked and rinsed in deionized distilled water. Determination of the quenching reagent conditional concentration factor (F), as defined subsequently in Results and Discussion, and its dependence with dialysis time, pH, calcium concentration and cadmium concentration were made using two different retentate solutions (pH 8.0-8.5) which were prepared to contain the following components: retentate solution A =

4×10^{-4} M $\text{Ca}(\text{NO}_3)_2$, 4×10^{-4} M boric acid-sodium borate buffer; retentate solution B = 2×10^{-3} M $\text{Ca}(\text{NO}_3)_2$, 4×10^{-4} M boric acid-sodium borate buffer. These solutions were meant to simulate the major cationic content of both the hardwater and softwater and without the precipitating or complexing effect due to carbonate presence. The initial pH of these solutions was about 8.5 and μL volumes of nitric acid were added to lower the desired pH between 8.0-8.5. Dialysis bags containing the quenching reagent (5 mL for the 1,000 MWCO and 20 mL for the 12,000-14,000 MWCO bags) were placed for specified amounts of time in 19 L volumes of these solutions which were contained in a polypropylene container (Nalgene). Filtered air (0.45 μ membrane filter and ascarite tube) vigorously bubbling at the rate of 1.7 L/min was used for stirring. Data on fraction dialyzed versus stirring rate for a fixed time period indicated that this rate was adequate. Dialysis experiments were also conducted in 720 mL volume tanks of the flow-through mini-diluter, run at a flow rate of approximately 15 mL/min/tank with air stirring of each tank solution at a rate of about 0.8 L/min (5,6). In both cases, samples of dialyzate and retentate were removed after various times of immersion. Each solution was transferred to an appropriate size and precleaned linear polyethylene bottle (Nalgene) and acidified to 0.5% v/v HNO_3 (Baker Ultrex) before being measured for total metal concentration by AAS.

AAS measurements were made according to standard procedures (11) and ISE measurements were made similar to other work (12,13).

RESULTS AND DISCUSSION

The main experimental approach was to determine equilibrium values for total cadmium in dialyzates as a function of appropriate variables. In hardwater, the cadmium species were primarily Cd^{2+} and soluble cadmium carbonate. Contribution from other soluble cadmium species such as CdOH^+ , CdCl^+ , and CdSO_4 was negligible since both the stability of their complexes and the concentration of their respective ligands was very low (5,10,13). Other components in the bioassay waters capable of interacting with cadmium were red clay and humic acid (Fig. 1), however no evidence was found indicating appreciable permeation of these types of substances through the dialysis membrane, which is in general accordance with other studies (1,4).

Possible problems that are normally associated with long equilibration times, such as precipitation or biological growths, can occur under certain conditions, therefore, the time for equilibration was minimized. Consequently, stirring with air bubbling was maximized to within the limits required for aeration in bioassays, in addition to using small enough size bags to maximize the membrane surface area/dialyzate volume ratio. This resulted in a relatively short dialysis time of approximately 4-5 h to attain 95% or greater equilibrium for the cadmium species under consideration (Fig. 2). Since SMI indicated that the 12,000 MWCO membranes were capable of higher dialysis rates, their bag diameter could be larger and still maintain a similar rate as the 1,000 MWCO membrane. This resulted in a comparatively larger dialyzate volume with which to work. The dialyzate volume was still less than ideal, but conversely it was also advantageous for this particular application because of the relatively small bioassay tank volume (720 mL). Correspondingly, less than 5% of the bulk tank constituents were lost to the dialyzate at any one time.

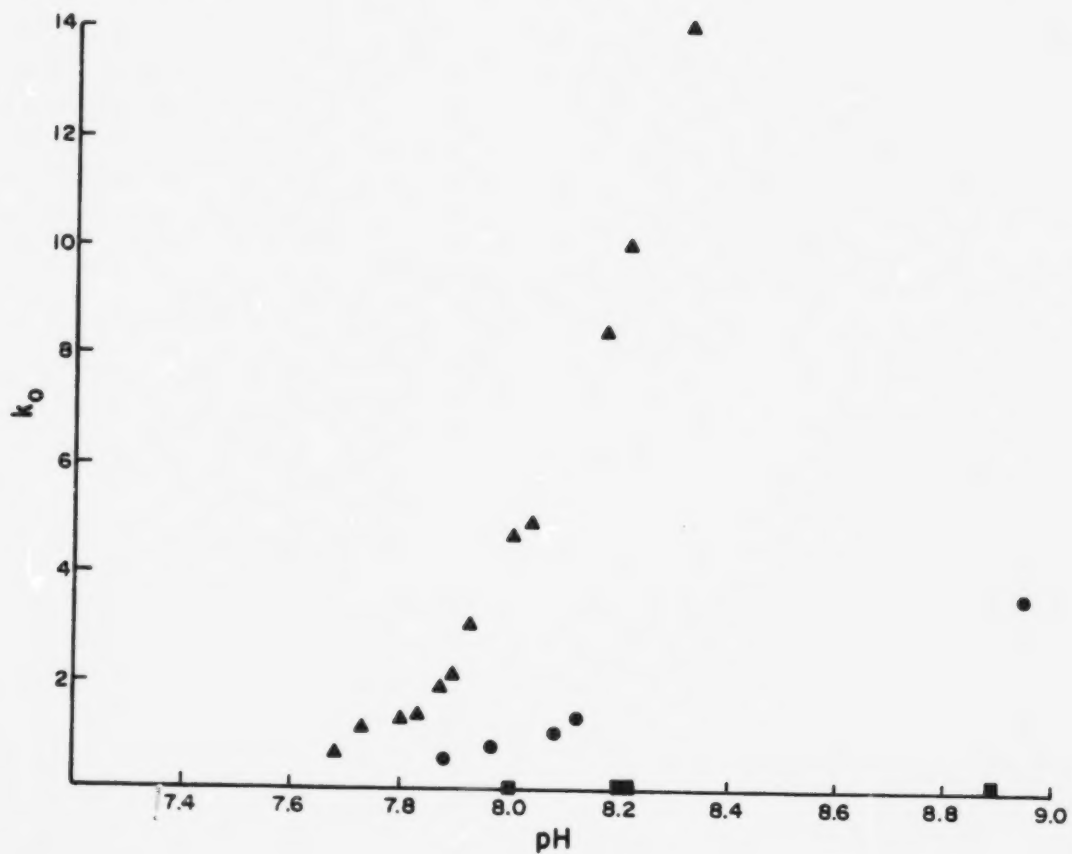


Figure 1. Water quality variables affecting the pseudo first-order rate constant (arbitrary units) for loss of free cadmium from solution.
 ▲ - hardwater + clay (90 NTU turbidity) + 10 mg/L Cd^{2+} , ● - hardwater + 10 mg/L Cd^{2+} , ■ - hardwater + clay (90 NTU turbidity) + humic acid (50 mg/L) + 10 mg/L Cd^{2+} .

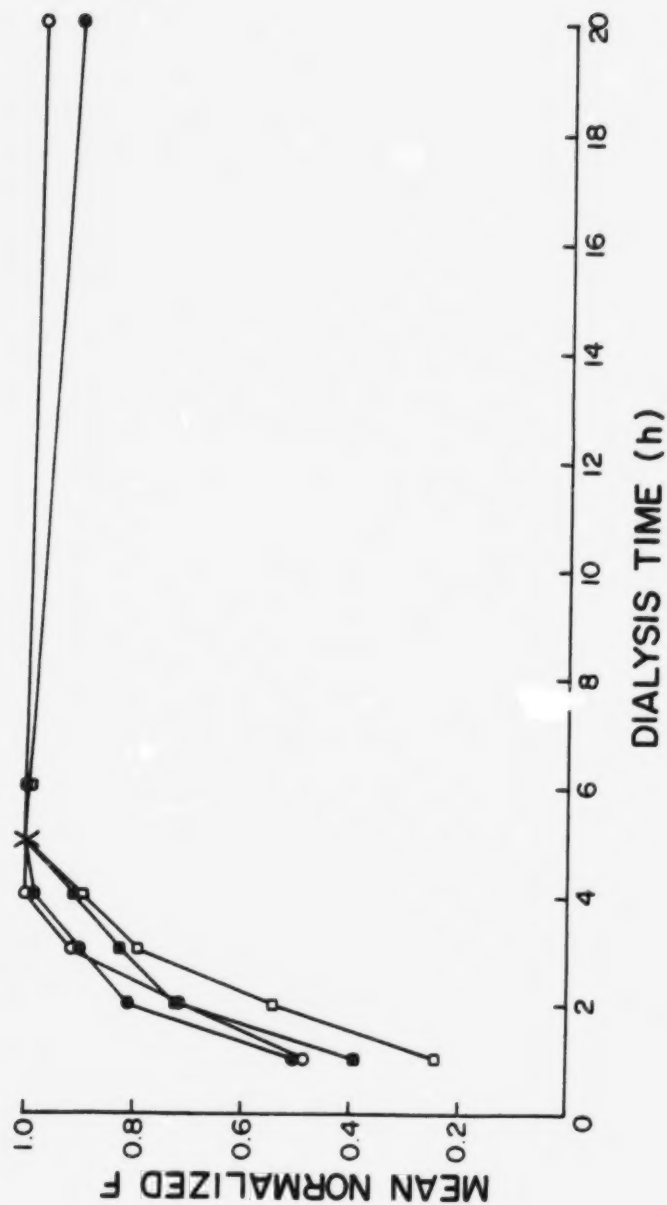


Figure 2. Change in mean 5 h normalized conditional concentration factor as a function of dialysis time for retentate solutions A and B.

Retentate solution A: ○ - 1,000 MWCO, ● - 12,000-14,000 MWCO;

Retentate solution B: □ - 1,000 MWCO, ■ - 12,000-14,000 MWCO.

X - data to which other data are normalized.

Reproducibility at High and Low Alkalinity. Table 1 presents replication data for 5 h dialyses of cadmium and other cations in the mini-diluter bioassay system, in addition to cadmium dialysis from retentate solution B. For these cases, deionized distilled water was used as the filling solution to compare the effect of various retentate solutions on reproducibility. Data are generally presented as the mean and relative standard deviation of ratios of total metal concentration in the dialyzate to total metal concentration in the unfiltered solution. In addition for just hardwater, the average ratio (and its relative standard deviation) of total cadmium concentration in the dialyzate to total cadmium concentration in the corresponding 0.45 μ filtrate is also given. Further, the means of the ratios of each filtered concentration to each corresponding total metal concentration are given for comparison. As expected for the softwaters, with little or no precipitation occurring, reproducible ratios close to 1 were obtained. These comparisons show that the filtrate and dialyzate ratios are very similar, suggesting a general equilibrium of cadmium and other dissolved components between dialyzate and retentate solutions. For hardwater, ratios significantly less than 1 were due to a contribution from particulate forms in the bioassay waters. In a typical hardwater flow-through bioassay system, Cd^{2+} concentrations of up to 1 mg/L were added to the high bicarbonate bearing bioassay waters. This resulted in the solubility product of cadmium carbonate being greatly exceeded with resultant precipitation continually occurring in the water column and sticking onto the surfaces of the tanks. Obviously, this process could also be occurring inside the dialysis bags, possibly giving rise to a significant source of imprecision and positive bias. It is these reasons that likely explain the unusually high average R value of 1.19 given for hardwater and the corresponding high relative

Table I. Reproducibility of 5 h dialyses in various carbonate alkalinity waters using deionized distilled water as the dialysis bag filling solution.

Retentate Water Type	Metal	R ^a	Percent Relative Standard Deviation	Number
Retentate Solution B, No carbonate alkalinity	Cd	1.02	6.1	12
Hardwater, 212 mg/L carbonate, alkalinity bioassay water	Cd	0.366	45.4	10
		1.19 ^b (0.312) ^c	34.0	10
Softwater, 48 mg/L carbonate alkalinity bioassay water	Cd	0.878 (0.948)	4.4	14
	Ca	0.912 (0.968)	1.0	4
	Mg	0.747 (0.816)	1.1	4
	Na	0.968 (0.948)	1.0	4

^a mean ratio of (total [metal] in dialyzate) / (total [metal] in retentate)

^b indicates mean ratio of (total [Cd] in dialyzate) / (total [Cd] in 0.45 μ filtrate)

^c parentheses indicate mean ratio of (total [metal] in 0.45 μ filtrate) / (total [metal] in unfiltered solution)

standard deviation (34%-45%), as presented in Table 1. Subsequent details will further describe this problem and how it might be avoided.

Quenching Effect of Humic Acid. Chemical kinetics studies (13) of Cd^{2+} added to hardwater, with and without added clay, indicated that the initial reaction rates exhibited pseudo first-order behavior with respect to loss of Cd^{2+} from solution and that they were greatly affected by a variety of other parameters, but most importantly humic acid presence (Fig. 1). In the absence of humic acid, observed pseudo first-order rate constants (arbitrary units) ranged from moderate to relatively high values, particularly at high pH and high clay concentration. However, under similar conditions with 50 mg/L humic acid present, observed rate constants were at near zero values over a range of pH conditions. In softwater, with or without clay or humic acid present, loss of Cd^{2+} from solution as a function of time was not observed. These specific observations demonstrated the problem and the likely benefit of employing humic acid in the dialyzate.

Effect of Variables on the Conditional Concentration Factor (F). The effect of using the quenching reagent preparation as the dialysis bag filling solution was investigated with regard to equilibration time, reproducibility, and possible accuracy of dialysis. Since this solution would undoubtedly bind cadmium ions, there would obviously be a natural tendency for cadmium to concentrate in the dialyzate. Therefore, it was necessary to determine this concentration factor and some factors affecting it. This information could permit calculation of the concentration (D) that would have normally dialyzed in the absence of the concentration effect of the quenching reagent.

It is appropriate to mention at this time that the experimental system studied (flow-through and fixed volume) had two noteworthy characteristics, namely, a) an effectively infinitely large retentate volume relative to the

dialyzate volume, and b) the humic acid in the quenching reagent contributed insignificantly to the overall ionic content of the dialyzate. Therefore, the phenomena commonly referred to as Donnan membrane equilibria (14) becomes insignificant in this case and should not be an additional factor complicating the interpretation of data. Definition of F may be attempted by first considering retentate media containing only dissolved cadmium species capable of equilibrating with the dialyzate, with F given by the following expression:

$$F = \frac{\text{total [Cd] in dialyzate}}{\text{total [Cd] in retentate}} = \frac{[\text{Cd}]_d}{[\text{Cd}]_r}$$

Retentate solutions A or B fulfill these requirements and therefore, the concentration of the species that are both inside and outside the membrane should be equal at equilibrium. For bioassay media, the concentration of other metals and ligands were considered negligibly low in concentration, except for cadmium, calcium, and bicarbonate. Calcium and bicarbonate concentrations were kept at a constant level, consequently concentrations of cadmium, pH, and dialysis time were studied as main parameters primarily affecting the value of F.

Figure 2 shows the effect of dialysis time (1-20 h) on values of F for retentate solutions A and B, all normalized to each corresponding mean 5 h F value representing a set of conditions. Conditions varied by using either 1,000 MWCO or 12,000 MWCO membranes and total cadmium concentrations in the range of <10-200 µg/L. As a result, very similar dialysis rates and equilibrium values were obtained regardless of the particular membrane. It can be seen that the value of F stabilized after 4 h and changed about 10% or less in the 4-20 h range. Reproducibility was in the range of 10% or less for the plateau region.

As anticipated, experiments that were conducted in high bicarbonate alkalinity bioassay water produced similar results with respect to dialysis rate and reproducibility (Fig. 3). Under actual bioassay conditions, a plateau was reached in 4-5 h. In addition, the improvement in reproducibility, that can be seen by comparing data in Figure 3 (error bars indicate standard deviation) to corresponding data in Table 1, strongly indicates that the high error associated with dialysis in this type of water can be significantly reduced by using an appropriate quenching reagent in the dialyzate.

Investigation of the effect of total cadmium concentration in the retentate versus total cadmium concentration in the dialyzate for retentate solutions A and B indicated that a non-linear relationship was operative. In contrast, a linear 1:1 relationship (to within 5%) was observed between 10 µg/L and 200 µg/L total cadmium when the dialysis bag filling solution was just deionized distilled water. Therefore, this observed non-linearity was attributed solely to the presence of the quenching reagent. Examination of the definitive relationships for applicable conditions provided the following expressions for retentate solution B containing negligible concentrations of complexing anions

$$F = \frac{[CdHA] + [Cd^{2+}] + [CdOH^+]}{[Cd^{2+}] + [CdOH^+]} = \frac{[Cd]_d}{[Cd]_r}$$

This may be approximated by

$$F = \frac{[CdHA] + [Cd^{2+}]}{[Cd^{2+}]}$$

since the contribution of $CdOH^+$ was less than 5%, according to equilibrium calculations and experimental data using the cadmium ISE (13). In high

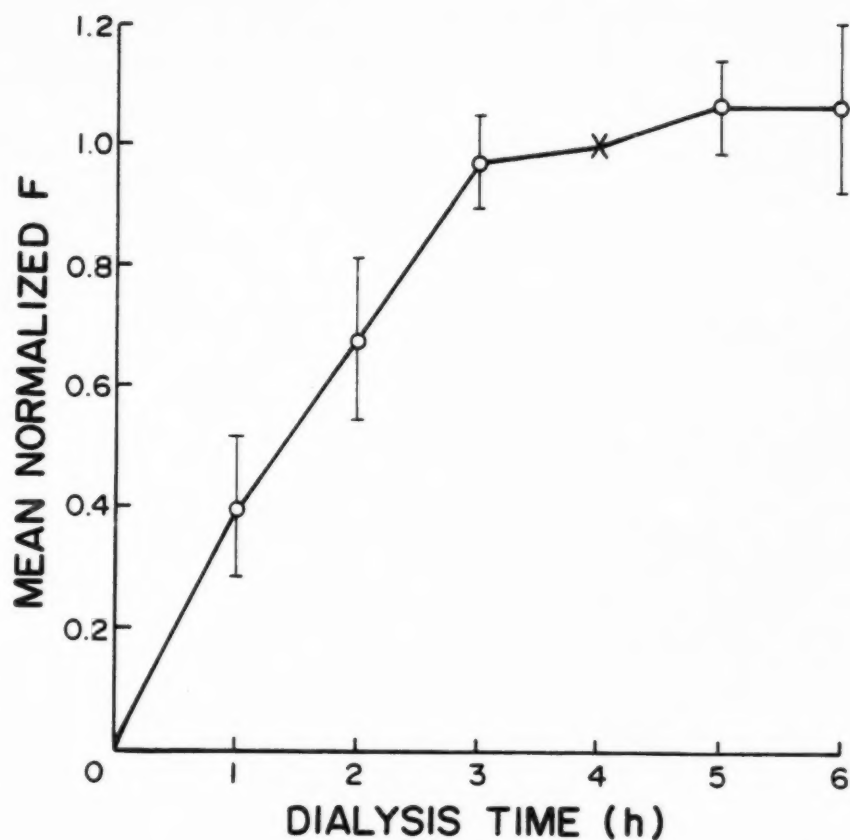


Figure 3. Change in mean 4 h normalized conditional concentration factor as a function of dialysis time for high bicarbonate alkalinity flow-through bioassay waters. X - data to which other data are normalized. The number of data points averaged for the 1, 2, 3, 5 and 6 hour periods were 7, 7, 2, 4 and 3, respectively.

alkalinity bioassay waters, the expression for the total dissolved cadmium concentration in the dialyzate (Cd_T) may be estimated by

$$[Cd_T] = [CdHA] + [Cd^{2+}] + [CdCO_3].$$

Since the relationship between $[Cd^{2+}]$ and $[CdHA]$ in the dialyzate is related by F and

$$[CdCO_3] = K_{CdCO_3} [Cd^{2+}] [CO_3^{2-}]$$

therefore

$$[Cd^{2+}] = \frac{[Cd_T]}{F + K_{CdCO_3} [CO_3^{2-}]}$$

For this system, the actual concentration (D) may be expressed as

$$D = [Cd_T] - [CdHA]$$

It follows that

$$D = [Cd_T] + \frac{(1-F) [Cd_T]}{F + K_{CdCO_3} [CO_3^{2-}]}$$

If cadmium monochloro and sulfate complexes contribute significantly, a more general expression would be

$$D = [Cd_T] + \frac{(1-F) [Cd_T]}{F + K_{CdCO_3} [CO_3^{2-}] + K_{CdCl} [Cl^-] + K_{CdSO_4} [SO_4^{2-}]}$$

All independent variables in this equation are known except for F . However, F may be approximated under specific known conditions. Figure 4 shows the value of F , both experimental and calculated values, as a function of the total dialyzate cadmium concentration for retentate solution B. Additional information on F as a function pH indicated that a change from 8.5 to 8.2 had no detectable effect on F , however major changes in either the Cd^{2+} or Ca^{2+} concentration could change F significantly. For example, the F value increased by approximately a factor of 1.4 in going from 2×10^{-3} M Ca^{2+} in retentate solution B to 4×10^{-4} M Ca^{2+} in retentate solution A, at pH 8.2 and 200 $\mu g/L$ Cd^{2+} . Since hardwater calcium concentrations were

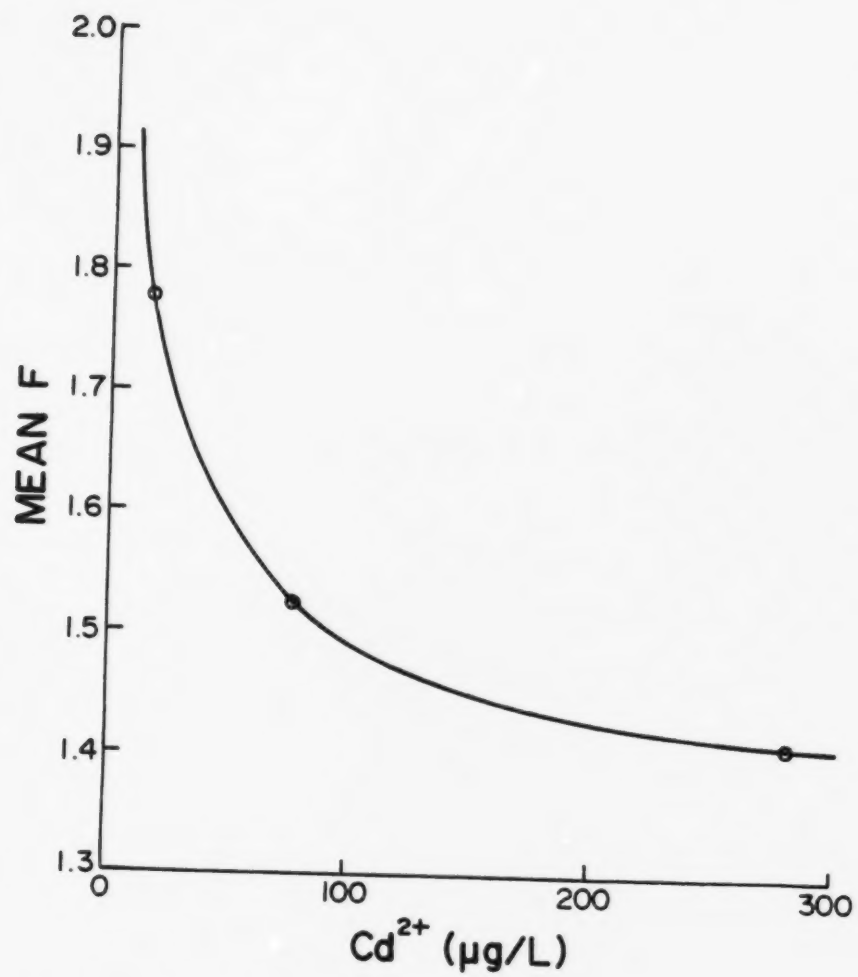


Figure 4. Calculated and mean experimental values of F for retentate solution B and the 1,000 MWCO membrane. — - calculated, O - experimental.

constant to better than 10%, this information indicated that F should not be significantly affected by minor fluctuations in the calcium concentration. In contrast, the effect of the Cd^{2+} concentration on F can be seen from experimental data given in Figure 4. In addition, it may be observed that the calculated curve from a third-order polynomial model of the form

$$F = A + B(\text{Ln}[\text{Cd}^{2+}]) + C(\text{Ln}[\text{Cd}^{2+}])^3$$

functioned adequately to approximate the non-linear experimental data for the 1,000 MWCO membrane. For these specific working conditions, values of A, B, and C were 2.505, -0.2726, and 0.002460, respectively. Similar results prevailed for the 12,000 MWCO membrane. The basic assumption was that the total retentate B cadmium concentration could be equated to the dialyzate Cd^{2+} concentration. In the bioassay systems, Cd^{2+} concentration in the dialyzates obviously was not known, however total cadmium in the dialyzate could be easily measured and used as a first-approximation in the equation for F. A value for D could be subsequently calculated and a better value for the Cd^{2+} concentration was then calculated from D. Through the process of successive approximations, better values of F and subsequently D and Cd^{2+} concentrations were calculated until a 0.1% convergence criteria was achieved. Use of lower values (0.001%) for the convergence criteria produced the same values obtained using the 0.1% value.

Comparison to Measurements via Cadmium ISE. The possible accuracy of this process was investigated by comparing, via a linear regression correlation ($\text{dialysis} = f(\text{ISE})$), the Cd^{2+} concentration determined by dialysis to the free cadmium concentration (Cd^{2+}) determined by ISE, in the range of 2 $\mu\text{g/L}$ to 132 $\mu\text{g/L}$ Cd^{2+} in hardwater bioassays. Figure 5 shows a plot of all comparisons for the 1,000 MWCO membrane. Resultant values of m, b, the correlation coefficient, and the number of comparisons were 0.84, 4,

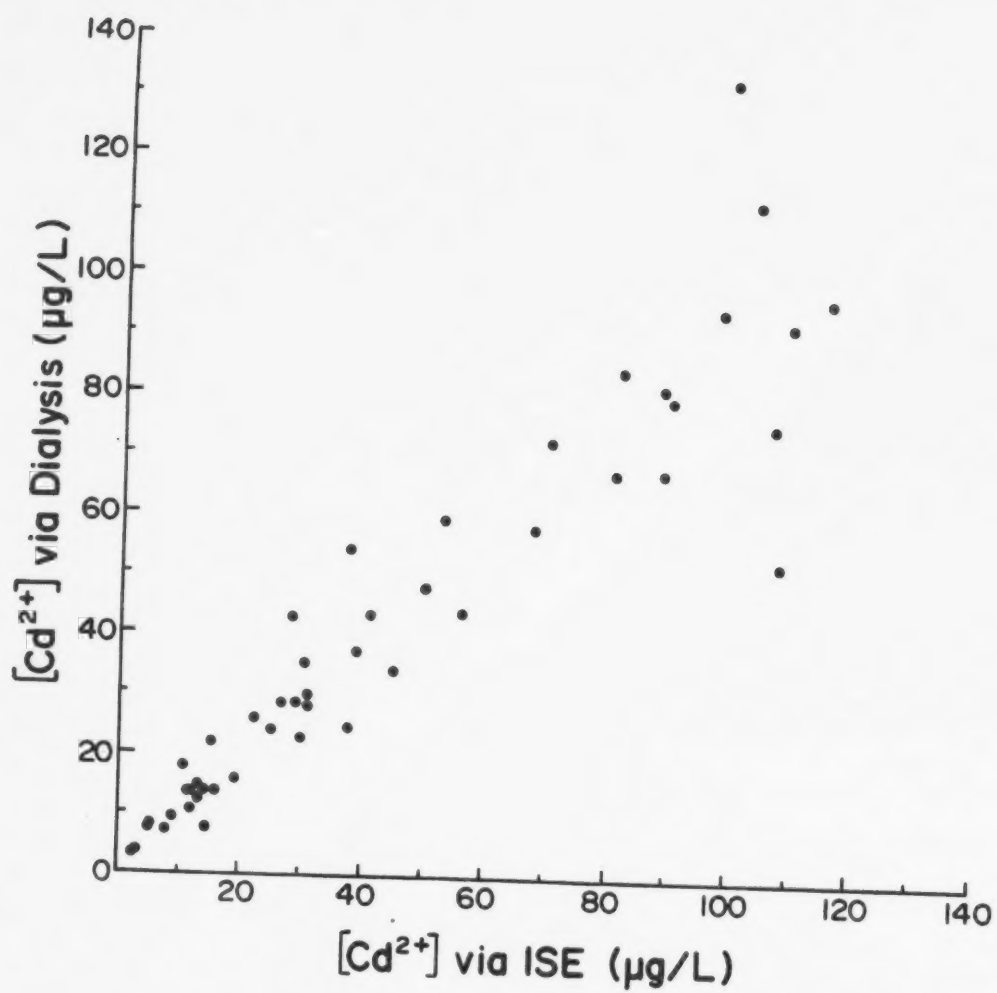


Figure 5. Correlation of values obtained by dialysis and ISE.

0.934, and 49, respectively. For the 12,000-14,000 MWCO membrane, the values were 0.83, 4, 0.966, and 32, respectively. As can be seen from Figure 5, both methods generally appeared to give quite similar values, although a statistical analysis of the data is not reported since the normal experimental error of these methods has not been adequately determined yet. However, a hint of discord between the application of these two methods can be seen through close visual inspection of the plot in Figure 5, which suggests that bias increases with concentration. Specifically, the slope value tends to decrease slightly. The reason for this is not clear, but it seems reasonable that the increased surface area in the tank presented by the outside surface of the dialysis bags may provide additional nucleation sites and slightly increase the rate of cadmium carbonate precipitation or adsorption onto the bag with increasing concentration and time of immersion. Since the cadmium dialysis and ISE measurements were done on the same sample, with ISE values obtained midway during the dialysis period, it seems plausible that the ISE values may tend to be higher than corresponding dialysis values for the higher concentrations. This effect would tend to slightly decrease the available cadmium in the relatively small volume bioassay tank (720 mL). In support of this contention, the data in Figure 5 was recalculated using the linear regression for concentrations which were 50 $\mu\text{g/L}$ and below. This resulted in values for m , b , the correlation coefficient, and the number of comparisons of 0.92, 2, 0.900, and 33, respectively. Although there were two apparent outliers at or above 100 $\mu\text{g/L}$, no reasonable explanation can be given for these occurrences.

It is possible, through further research, that the usefulness of this novel approach may extend to other areas such as titrations of natural

waters, as described by Truitt and Weber (3,4). In addition, more suitable quenching reagents may be found in the process.

LITERATURE CITED

- 1) Benes, P. Semicontinuous Monitoring of Truly Dissolved Forms of Trace Elements in Streams Using Dialysis In Situ I. Principle and Conditions. *Water Res.* 1980, 14, 511-513.
- 2) Rainville, D. P.; Weber, J. H. Complexing Capacity of Soil Fulvic Acid for Cu^{2+} , Cd^{2+} , Mn^{2+} , Ni^{2+} and Zn^{2+} Measured by Dialysis Titration: A Model Based on Soil Fulvic Acid Aggregation. *Can. J. Chem.* 1982, 60, 1-5.
- 3) Truitt, R. E.; Weber, J. H. Determination of Complexing Capacity of Fulvic Acid for Copper(II) and Cadmium(II) by Dialysis Titration. *Anal. Chem.* 1981, 53, 337-342.
- 4) Truitt, R. E.; Weber, J. H. Copper(II)- and Cadmium(II)-Binding Abilities of Some New Hampshire Freshwaters Determined by Dialysis Titration. *Environ. Sci. Technol.* 1981, 15, 1204-1208.
- 5) Benoit, D. A. U.S. Environmental Protection Agency, Duluth, MN, Personal Communication, 1981-1983.
- 6) Benoit, D. A.; Mattson, V. M.; Olson, D. M. A Continuous-Flow Mini-Diluter System for Toxicity Testing. *Water Res.* 1982, 16, 457-464.
- 7) Lemke, A. E. A Water Hardener for Experimental Use. *J. Am. Water Works Assoc.* 1969, 61, 415-416.
- 8) Poldoski, J. E.; Glass, G. E. Anodic Stripping Voltammetry at a Mercury Film Electrode: Baseline Concentrations of Cadmium, Lead, and Copper in Selected Natural Waters. *Anal. Chim. Acta* 1978, 101, 79-88.
- 9) Poldoski, J. E.; Leonard, E. N.; Fiandt, J. T.; Anderson, L. E.; Olson, G. F.; Glass, G. E. Factors in the Determination of Selected Trace Elements in Near-Shore U.S. Waters of Lakes Superior and Huron. *J. Great Lakes Res.* 1978, 4, 206-215.

- 10) Weiler, R. R.; Chawla, V. K. Dissolved Mineral Quality of Great Lakes Waters. Proc. 12th Conf. Great Lakes Res., Internat. Assoc. Great Lakes Res. 1969, 801-818.
- 11) U.S. Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes, March 1979, EPA-600/4-79-020.
- 12) Poldoski, J. E.; Glass, G. E. Considerations of Trace Element Chemistry for Streams in the Minnesota-Ontario Border Area. Proc. Internat. Conf. on Heavy Metals in the Environment, Hutchinson, T. C., Ed., Toronto, Ontario, Canada, Oct. 27-31, 1975, 901-922.
- 13) Poldoski, J. E. U.S. Environmental Protection Agency, Duluth, MN, Unpublished work, 1981-1983.
- 14) Moore, W. J., "Physical Chemistry", 3rd ed.; Prentice-Hall: Englewood Cliff, N.J., 1962; pp. 760-761.